PHYSICO-CHEMICAL STUDIES ON THE COORDINATION COMPOUNDS OF TRANSITION METALS WITH LIGANDS HAVNIG N/P/S/O AS DONOR SITES

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

CHEMISTRY

BY

SAJI P. V.

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

1991

DEDICATED
TO
MY PARENTS

DIVISION OF INORGANIC CHEMISTRY
DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202002 (INDIA)

MOHAMMAD SHAKIR
M. Sc., Ph. D, (Alig.)
Senior Lecturer

Phone office 25515
Dated... 25/6/1992

CERTIFICATE

Certified that the work embodied in this dissertation entitled 'Physico-Chemical Studies on the Coordination Compounds of Transition Metals with Ligands having N/P/S/O as donor Sites' is the original research work carried out by Mr. P.V. Saji, under my supervision. This work is suitable for the submission of the award of M.Phil. Degree of Aligarh Muslim University, Aligarh.

(Dr. MOHAMMAD SHAKIR)

SAJI P. V.,Msc.
Department of Chemistry
Aligarh Muslim University
Aligarh - 202002.

Dated: 07/07/04

ACKNOWLEDGEMENTS

It is indeed a great pleasure to express my gratitude to Dr.M.Shakir for his kind guidance, continuous encouragement and stimulating discussion throughout my work.

I am extremely beholden to my parents for their affectionate encouragement, assistance and interest in my academic pursuits.

Prof.M.A.Rauf Chairman, Department of Chemistry is thanked for providing necessary facilities.

I am indebted to my laboratory colleagues for their help, cooperation and encouragement. Thanks are also due to Dr. S.I Khan for providing spectral facilities at CDRI, Lucknow.

I feel pleasure to express the sincere thanks to Mr. M. Ayub Khan for typing this dissertation.

SAJI P.V

C O N T E N T S

INTRODUCTION

INTRODUCTION

Recent interest in metal compounds containing coordinated heterocycles[1-3] has led researchers to synthesize a number of pyrazole and substituted pyrazole derivatives as potential complexing agents. The pyrazoles, Rpz (R = H, alkyl or aryl groups) [Fig. (1)] are thermally and hydrolytically very stable moieties. As a ligand, it coordinates to metals and metalloids through pyridyl nitrogen N(2). A survey of literature has revealed a variety of complexes of these 2-monohaptopyrazoles (Rpz)[4-7]. However, deprotonated pyrazole becomes the pyrazolide ion [Fig. (II)] may coordinate through both nitrogen atoms.

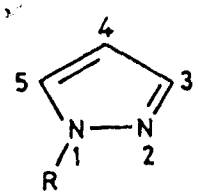


Fig. (I)

(R = H, Me, Ph)

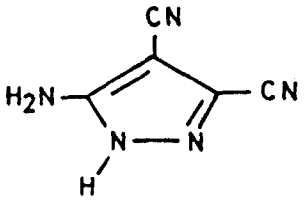


Fig. (II)

The simplest and most thoroughly studied types of pyrazole complexes are $[M(Rpz)_nX_m]$ where M = transition metals, Rpz = 2-monohaptopyrazoles, X = counter ions, m = valance state of the transition metals, usually divalent. These complexes are

prepared by the reaction of metal salts with pyrazoles (Rpz) in neutral or slightly acidic media. However, formation of pyrazolide polymers $[M(pz)_2]_n$, predominates under basic conditions as given below:

$$MX_2 + mHpz \longrightarrow M(Hpz)_mX_2 \quad \ldots (1)$$

$$MX_2 + 2pz^- \longrightarrow [M(pz)_2]_n + 2X^- \quad \ldots (2)$$

The complexes in equation 1 are reported[4-7], to coordinate via pyridyl nitrogen N(2) of the five membered ring. This has been further confirmed by X-ray crystallography[8-12]. However the number of pyrazoles coordinated to the metal ions has been reported to be influenced by

1. Coordinating ability of the counter ion : Maximum coordination has been reported in the complexes of the type $[M(Hpz)_6]X_2$ [M = Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II)][4,13], when counterion X = NO_3^-, BF_4^- and ClO_4^-. However, if counterion X = Cl, Br, I, the complex formed are $[M(Hpz)_4]X_2$ [M = Ni(II), Co(II) and Fe(II)][4]. The structure of $[Ni(Hpz)_6]\ (NO_3)_2$, $[Ni(Hpz)_4Cl_2]$ and $[Ni(Hpz)_4Br_2]$ have been established by X-ray crystallography[8-12]. In $[Ni(Hpz)_6]\ (NO_3)_2$ the Ni(II) ion lies at the center of a nearly regular octahedron of coordinated N atoms. In the complexes $Ni[(Hpz)_4X_2]$ the halogens are coordinated to the Ni placing it again in an octahedral environment. The

pyrazole rings are oriented vertically with respect to the plane defined by the Ni atom and the four coordinated nitrogen and there exists a hydrogen bond between the N(1) and the halogen in these compounds.

2. Nature of the metal ion : It has been reported that Cu(II) never give the complexes of the type $[Cu(Hpz)_6]X_2$ under any conditions, rather it produces only tetracoordinate complexes of the type $[Cu(Hpz)_4X_2]$ regardless of the nature of counter anion X (Cl^-, Br^-, BF_4^-, ClO_4^-, SO_4^-, NO_3^-)[4,14,15]. The presence of 4-substituents such as Cl, Br, NO_2 or of 1-Me did not alter the maximum CuL_4^{2+} stoichiometry[16].

3. Substitution on the pyrazole ring : A substituent in the position (3) introduces steric hindrance and makes it difficult to have six 3-substituted pyrazoles coordinated via N(2) to a metal ion. This difficulty can be circumvented by coordination through a tautomeric 5-substituted structure, where steric hinderence is minimized. The highest apparent coordination number for a variety of transition metal ions (Mn, Fe, Co, Cd) has been reported[5] in structures of the type $[M(H_3Mepz)_7]\ (ClO_4)_2$, although the seventh pyrazole is regarded as being in the second coordination sphere. By contrast H3,5-Me_2pz which has both positions adjacent to the nitrogens substituted with methyl groups forms only complexes of the type $[M(H3,5Me_2pz)_4X_2]$[5,17].

However, in 4-methylpyrazole where the methyl group is far from the coordination site behaves like pyrazole itself[5].

Electronic spectra taken in solution[4] or on single crystals of $Ni(Hpz)_6^{2+}$ complexes[18] give ligand field, Dq value of 1065-1080 cm^{-1} and indicate that pyrazole occupies a position similar to that of pyridine or ammonia in the spectrochemical series. A more detailed study of electronic spectra of the complexes $M(H5Mepz)_2X_2$ (M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) and X = NO_3^-, Cl^-, Br^-, I^-, ClO_4^- and BF_4^-) showed considerable distortion from octahedral symmetry. This was attributed to hydrogen bonding between the ligand and the anions[8]. Infrared and Raman spectra of these complexes show the NH vibration to be strongly dependent on hydrogen bonding which was found to be greatest with Cl^- followed by Br^-, I^-, NO_3^- and BF_4^-, while no hydrogen bonding was observed with ClO_4 anion.

Apart from complexes of the first-row transition metals pyrazole complexes to ruthenium in several oxidation states have been investigated. The blue solution of Ru(II), when treated with pyrazole or 3,5-dimethylpyrazole, produced species such as $[RuL_3Cl_3]^-$, $RuCl_2L_3.(H_2O)$, etc., characterized by physicochemical analyses and conductivity data[19]. Pyrazole reacted with $RuCl_3$ to form the anion $[Ru(Hpz)OHCl_4]^-$ gave an insoluble silver salt and the neutral species $Ru(Hpz)_3Cl_3$[20]. Complexes of the type L_2AgNO_3 and $L_2(HgCl_2)_3$, where L = 3(5)-Methylpyrazole have

also been reported[21]. It has been reported that 5-ethynyl-1-methylpyrazole forms a complex with $NiBr_2$, but 3-ethynyl-1-methylpyrazole does not, because of steric reasons.

In addition to complexing with simple transition metal ions, pyrazoles have been reported to coordinate with diverse organometallic species. Thus, the reaction of pyrazole with $(C_5H_5)CoI_2CO$ results in the displacement of CO and the formation of $C_5H_5CoI_2(Hpz)$ as an air-stable green solid[22]. Simple coordination by pyrazole to relieve coordinative unsaturation has been reported[23] for $[H_2B(pz)_2Mn(CO)_3]$. It was found that the addition of pyrazole gives rise to an inert gas configuration.

The reaction of $Fe(CO)_5$ with 3,5-dimethylpyrazole is reported[24] to give the air-sensitive $[(H3,5\text{-}Me_2pz)_2FeCO]$ as a pink solid. A π-bonded sandwich structure has been tentatively proposed for this compound, this, however, seems unlikely. The above result contrasts with the reaction of iron pentacarbonyl with pyrazole itself, where $[Fe(pz)_2]_n$ is obtained[24]. The dimeric compounds $[pzFe(CO)_3]_2$ and $[3,5\text{-}Me_2pzFe(CO)_3]_2$, which may have a metallocyclic structure have also been reported[25]. The reaction of 3,5-dimethylpyrazole with chromium hexacarbonyl yields only the $[LCr(CO)_5]$ at any reactant ratios, while with tungsten hexacarbonyl either $LW(CO)_5$ or $L_2W(CO)_4$ may be obtained[26].

The reaction of anhydrous $CuBr_2$ with 3,5-diphenylpyrazole in a 1:2 ratio in t.h.f. yields bis(3,5-diphenylpyrazole) dibromocopper (II)[27]. Hexakis (μ-3,5-diphenylpyrazolato-N,N') hexagold (I) was obtained from the reaction of $Au(PPh_3)Cl$, AgO_2CPh, and sodium 3,5-diphenylpyrazolate in t.h.f.[27]. The monomer, both trimers and hexamer have been characterized by X-ray crystallography. The synthesis and characterization of the complexes of 5-amino-4-cyanopyrazole with various transition metal chlorides and their triphenyl phosphine derivatives[28a,28b] have been reported recently.

The ability to lose the 1 proton and to function as a uninegative, exobidentate 1,2-dihapto ligand of C_{2v} symmetry is a characteristic feature of pyrazole. The geometry of pyrazolide ion permits it to act as a bridge between two identical or dissimilar metals or metalloids. Polymeric complexes containing the exobidentate 1,2-dihaptopyrazolide ligand have been known since 1889, when polymeric metal complexes containing a single pyrazolate bridge have been reported[29]. The synthesis of polymeric $[Ag(pz)]_n$ compounds has been reported[30] as well as the use of a $[Ag(pz)]_n$ electrode for the determination of stability constants of other metal pyrazolates. The synthesis of an at least trimeric complex of the type $[Ag(pz)]_n$ has also been reported[31]. Recently dimeric complexes of 1,2-dihapto-4-cyano-5-amino pyrazolide ion have been reported from this laboratory[32].

There exist three principal types of neutral heterocyclic pyrazole derivatives containing two or four coordinate boron atoms. The pyrazoboles of type $R_2B(pz)BR'_2$ as shown in Eq. 3 have been known for more than 2 decades.

$$R_2B(pz)_2^- + BR'_2 \longrightarrow R_2B(pz)_2BR_2' + X' \quad \ldots(3)$$

Triply bridged pyrazaboles of type [Fig. (III)] with X = -OBRO- were accidentlly discovered in recent studies of the interaction of boroxins, $(-RBO-)_3$ with pyrazole[33,34]. In addition several dibora monocations of the structural type [Fig. (III)] where X = pz, have been reported[33,35,36].

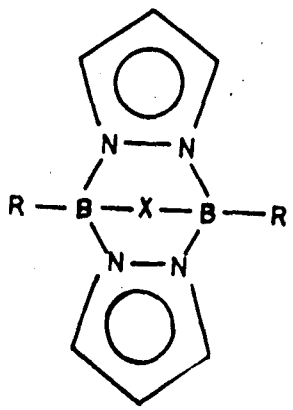


Fig. (III)

Compounds of type [Fig.(IV)] were obtained from the reaction of borazines, $(-RBNR'-)_3$, with pyrazole, and only three such species (X = NHR') have been reported[37]. Only most recently, four additional species containing the central B_2N_2X ring have been obtained from the reaction of bis(diorganoboryl)chalcogenides, $(R_2B)_2X$ (R = C_2H_5, X = O; R_2 = 1,5-C_8H_{14}, X = O or S or Se) with pyrazole. The mode of attack finds support in the reactons of Hpz with various other heterocycles containing two boron atoms[38] where the NH moiety was readly displaced to give the triply

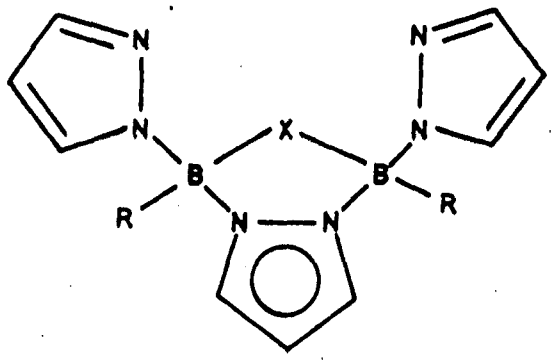


Fig.(IV)

bridged pyrazabole [Fig.(V)] as shown in eq. 4.

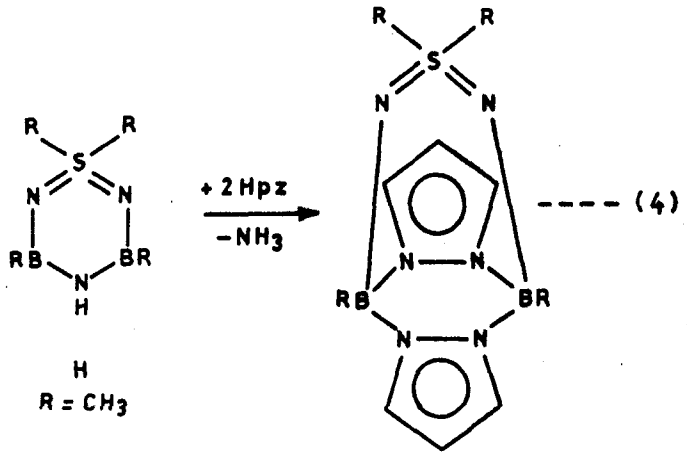


Fig. (V)

The uninegative tridentate hydrotris (pyrazol-1-yl) borate anion [Fig. (VI)] has become a useful ligand for the transition elements[39]. M. Dolores and co-workers have recently used the potassium salt of [Fig. (VI)] to prepare the alkylidyne tungsten

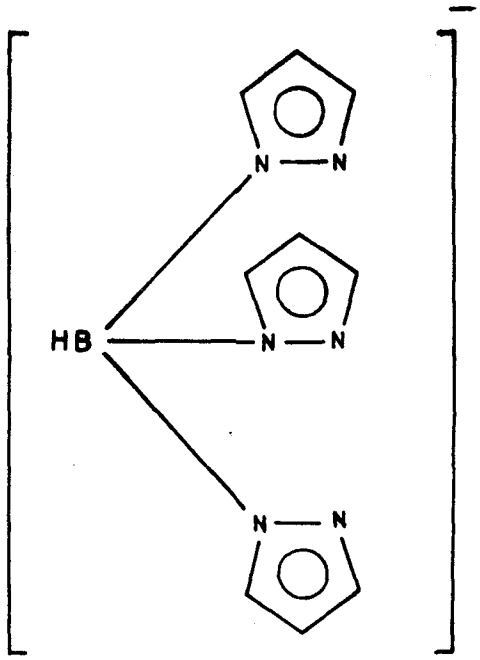


FIG. (VI)

complexes [W(=CR)$(CO)_2$ $HB(pz)_3$] [R = C_6H_4Me-4 or Me], $HB(pz)_3$ = hydrotris(pyrazole-1-yl)borate], and have used these species as precursors for the synthesis of compounds wherein tungsten forms bonds with other transition metals[40]. Structural, spectral and magnetic investigation of various types of compounds and their isomers isolated from the system Cu(II) $-C(CN)_3-$ pyrazole have been reported recently[41].

In complexes with f- block elements, bidentate bonding [Fig.(VII)] has been observed in some cases[42-44], which is contrary to the d-block elements. The possibility of π (η^5)-bonding has been considered but not established[45]. A large class of MCp_3X compounds (M = lanthanide or actinide) are formally 10-coordinate, Fischer and coworkers have reported 11-coordinate $UCp_3(NCS)$ (CH_3CN)[46]. Organouranium complexes of pyrazole of the type $U(C_5Me_5)_2$ $Cl_2(C_3H_4N_2)$, $U(C_5Me_5)Cl(C_3H_4N_2)$ have been prepared by the reaction between $U(C_5Me_5)_2Cl_2$ and pyrazole $C_3H_4N_2$, in t.h.f.[47] and the structure of the complex was confirmed through X-ray studies. A recent attempt to prepare $Ln(dmpz)_3$, of the bulkier 3,5-dimethylpyrazolate(dmpz) ligand

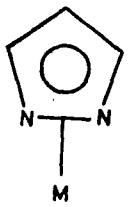


Fig. (VII)

from $LnCl_3$ and Na(dmpz) gave$[Ln_3(\mu\text{-dmpz})_6(\eta^2\text{-dmpz})_3(\mu_3\text{-O})Na_2L_2]$ [Ln = Y, Ho, Yb or Lu; L = H(dmpz) or t.h.f.] Clusters[44]. The tris(pyrazolato)neodymium(III) complexes, NdL_3 (L = pz or dmpz) were prepared and confirmed through X-ray analysis.

$$2Nd + 3Hg(C_6H_5)_2 + 6HL \longrightarrow 2NdL_3 + 6C_6F_5H + 3Hg \quad \ldots\ldots (5)$$

in good yield by reaction of neodymium metal with bis penta-fluorophenyl)mercury and either pyrazole or 3,5-dimethylpyrazole in t.h.f. at room temperature as shown in eq. 5.

PRESENT WORK

PRESENT WORK

The present project deals with the ligational behaviour of a substituted pyrazole ligand, 3,4-dicyano-5-aminopyrazole, $H3,4(CN)_2 5NH_2 pz$. The aim to select such a substituted pyrazole is to investigate the effect of substituted donor groups, CN and NH_2 on the expected site of coordination i.e. pyridyl nitrogen N(2) of the pyrazole ring. The reaction of the ligand, $H3,4(CN)_2 5NH_2 pz$ with anhydrous transition metal chloride MCl_2 [M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)] have been carried out in 1:4 molar ratio (metal to ligand) at room temperature, resulting in the isolation of solid mass of the type $[ML_4Cl_2]$ (L = $H3,4(CN)_2 5NH_2 pz$) where the number of pyrazole rings attached to the metal ions are consistent with the reported nature of the metal ions[4,14-16] and counter ions[4,7].

The exact site of coordination of the ligand $H3,4(CN)_2 5NH_2 pz$ to the metal ions in presence of three strong donor substituents, two cyanide(-CN) groups and one amino ($-NH_2$) group and the overall geometry of the complexes has been confirmed on the basis of physico-chemical methods. The bands observed in the i.r. spectra of the compounds prepared in the present project strongly suggest the coordination of $H3,4(CN)_2 5NH_2 pz$ via pyridyl nitrogen N(2) even in presence of the strong donor groups similar to that reported for the complexes of $H3,5\text{-}Me_2 pz$, $R3Me5NH_2 pz$

and $H4CN5NH_2pz$ with variety of trialkyl boranes and metal salts[4-12,28a,28b,32].

The reaction of $H3,4(CN)_25NH_2pz$ with triphenylphosphine derivatives of transition metal chlorides $[M(PPh_3)_2Cl_2]$ [M = Mn(II), Co(II), Ni(II), Cu(II)] in 1:4 molar ratio at room temperature results in the formation of solid products. The i.r. spectra of these compounds, do not contain bands characteristic of Ph_3P moiety suggesting the complete removal of coordinated Ph_3P leading to the formation of the complexes with similar stoichiometry, $[ML_4Cl_2]$ analogous to that formed from their corresponding anhydrous metal chlorides such that $H3,4(CN)_25NH_2pz$ is coordinated via pyridyl nitrogen N(2). The mother liquor evaporated under vacuum left an equivalent amount of Ph_3P as microcrystalline mass.

The ligational behaviour of this ligand has also been checked with metal chlorides of the group IIB metals MCl_2 and their triphenyl derivatives, $[M(PPh_3)_2Cl_2]$ [M = Zn(II), Cd(II), Hg(II)] by incorporating their reactions under similar reaction conditions observed for transition metal chlorides or their triphenylphosphine derivatives. The solid products thus formed have been isolated and it has been found in all the complexes that the ligand is coordinated through pyridyl nitrogen N(2).

The i.r. spectra of the complexes derived from triphenylphosphine derivatives donot contain bands characteristic of Ph_3P suggesting total removal of Ph_3P. In brief it is concluded that the interaction of $H3,4(CN)_2 5NH_2pz$ as a ligand with divalent metal ions or their triphenyl phosphine derivatives acts as 2-monohapto ligand.

In view of the ability of the pyrazole ligand[29] to lose the 1 proton and to function as an uninegative, exobidentate, 1,2-dihapto ligand called pyrazolide ion of C_{2v} symmetry, it is proposed to synthesize and characterize the complexes of 3,4-dicyano-5-aminopyrazolide ion $[3,4(CN)_2 5NH_2pz]^-$ with metal (I) chlorides and the corresponding triphenylphosphine derivatives, $[M(PPh_3)_3X]$ (M = Co, Cu, Ag, X = Cl). The reaction of ammonical solution of metal (I) chlorides, MCl with $H3,4(CN)_2 5NH_2pz$ results in the isolation of colorless highly insoluble, polymeric products presumbly of the type $[M(3,4(CN)_2 5NH_2pz)]_n$ [M = Cu(I) and Ag(I)]. The existances of pyrazolide ion in these compounds has been confirmed by disappearance of νN-H stretching vibration in the i.r. spectra of these complexes.

S. Trofimenko reported that the polymerization may be avoided in presence of appropriate encapping group leading to the formation of metallocycles. Therefore, the ammonical solution of triphenylphosphine derivatives of Co(I), Cu(I) and

Ag(I), $[M(PPh_3)_3X]$ is reacted with $[H3,4(CN)_25NH_2pz]$ affords the isolation of solid products, having the stoichiometry as $[M(PPh_3)_2L]_2$ where Ph_3P group acts as the endcapping ligand. The involvement of both the nitrogen pyridyl N(2) and pyrrolic N(1) in these compounds has been confirmed by the disappearance of νN-H stretching vibration suggesting deprotonation of $H3,4(CN)_25NH_2pz$ and resulting the formation of uninegative, exobidentate 1,2-dihapto-3,4-dicyano-5-aminopyrazolide ion $[3,4(CN)_25NH_2pz]^-$.

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

There are several physico-chemical methods available for the study of coordination compounds. A brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work is given below :

1. Infrared Spectroscopy
2. Magnetic Susceptibility Measurements
3. Ultraviolet and visible (Ligand Field) Spectroscopy
4. Conductometric Measurements.
5. Elemental Analysis

The frequency associated to certain groups of atoms is called group frequency. These frequencies are characteristic of the group irrespective of the molecule in which these groups are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule. The wave number i.e. the number of waves per centimeter is used to characterize the radiation. The infrared and far infrared spectra were recorded as KBr discs on a Perkin-Elmer - 621 (4000-200 cm^{-1}) spectrophotometer in the chemistry department of Guru Nanak Dev University, Amritsar.

In the following paragraphs, only those frequencies which are pertinent to the discussion of the newly synthesized compounds will be discussed.

Pyrazole Ring Vibrations :

The assignments for various bands were obtained by studying the infrared spectra of the 3,4-dicyano-5-aminopyrazole ligand and compared with the reported[7,28a,28b,48,49] spectra of the pyrazole and its substituted derivatives. The important groups vibration of the pyrazole ring and the substituted groups are briefly discussed as follows :

N-H Stretching Frequency :

The N-H stretching vibrations occur in the region 3500-3300 cm^{-1} in dilute solution. The N-H stretching band shifts to lower value in the solid state due to extensive hydrogen bonding. The νN-H (pyrrolic) stretching vibration appear at a lower wave length 2920 cm^{-1} which is attributed to intra and inter molecular hydrogen bonding[7,50,57]. The N-H bending vibrations have been reported[52] for many solid pyrazole. However in the present ligand the N-H bending vibration have not been seen.

NH_2 Group Frequency :

A multiplet appeared in the region 3300-3400 cm^{-1} followed by a strong band at 1610 cm^{-1} may reasonably be assigned to NH_2 group.

-C = N Stretching Frequency

A medium band at 1490 cm^{-1} in the i.r. spectrum of

$H3,4(CN)_2 5NH_2pz$ may be attributable to νC=N stretching vibration consistent with benzopyrazole[53] which has got a negative shift ($\sim$5 - 15 cm^{-1}) on coordination to metal ions.

-C ≡ N Stretching Frequency :

A very strong absorption band obtained in the frequency region (2250-2255 cm^{-1}) as reported[54-57] for the free -C ≡ N group.

M - N Stretching Frequency :

The M-N stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. Several amine complexes exhibited the metal-nitrogen frequencies in the region 300-420 cm^{-1}. In the present complexes the formation of a strong band in the region (225-235 cm^{-1}) consistent with the reported[57-59] analogous.

M - Cl Stretching Frequency :

Metal-halogen stretching vibrations are generally observed in the low frequency infra red region (400-200 cm^{-1})[60]. In the present complexes the far i.r. spectra of the chloro complexes reveal some bands with medium intensity at 280-290 cm^{-1}.

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The magnetic susceptibility measure-

ments were carried out by using a Faraday balance at 25°C in the chemistry department of Guru Nanak Dev University, Amritsar. Molecular weights of the compounds were determined by Rast method[61]. The electrical conductivities of 10^{-3}M solution in DMSO were obtained on a systronics type 302 conductivity bridge thermostatted at 25 ± 0.05°C. Reflectance spectra of the solid samples were recorded on a Carl-Zeiss VSU-2P Spectrophotometer using MgO as calibrant and electronic spectra in DMSO were recorded on a Pye Unicam-8800 Spectrophotometer.

The chemical analysis helps in assigning the stoichiometric composition of the ligand as well as its metal complexes. Carbon hydrogen and nitrogen analyses were carried out from the micro-analytical laboratory of the Central Drug Research Institute (CDRI) Lucknow. The estimation of chlorine was done gravimetrically[62] and the metals were estimated volumetrically[63]. For the metal estimation, a known amount of complex was decomposed with a mixture of nitric/perchloric/sulphuric acids in a beaker. It was then dissolved in water and made upto a known volume so as to titrate it with standard EDTA. For chlorine estimation, a known amount of the sample was treated with fusion mixture (KNO_3 and K_2CO_3).

EXPERIMENTAL

EXPERIMENTAL

Materials and Methods

Reagents used - Triphenylphosphine, (Ph_3P) (Sisco), $CrCl_2.H_2O$, $MnCl_2 4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $FeCl_2.6H_2O$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, AgCl (all BDH) reagents commercially available. The ligand 3,4-dicyano-5-aminopyrazole was prepared by the reported method[64]. The solvents, tetrahydrofuran, dimethylsulfoxide and ethanol were commercially available pure samples and were dried before use by the reported method[65].

Dehydration of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$[66]

Dehydration of $CoCl_2.6H_2O$

$CoCl_2.6H_2O$ powder (10 gm) was placed in a R.B. flask fitted with a ground joint and was covered with $SOCl_2$. The mixture was refluxed for 3 hrs. The excess $SOCl_2$ was evaporated on a steam bath. The $SOCl_2$ which adjoined to the product was removed by repeated evaporation of the flask.

Dehydration of $NiCl_2.6H_2O$

10 gm of $NiCl_2.6H_2O$ was taken in a round bottom flask and then mixed with 60 ml $SOCl_2$ and refluxed for 1 hrs. The dehydrated salt were collected by filtration and dried in vacuo giving yellow crystalline solid.

Dehydration of $CuCl_2.2H_2O$

Hydrated cupric chloride (5 gm) was refluxed with 50 ml $SOCl_2$. The excess of $SOCl_2$ was removed by distillation and evaporation of residual solvent in vaccum.

Dehydration of $MnCl_2.4H_2O$

10 gms of Mn(II)chloride tetrahydrate was refluxed with 50 ml of acetic anhydride for 3 hrs. The compound then filtered, washed several times with acetic anhydride followed by $SOCl_2$ and vacuum dried.

Dehydration of $CrCl_2.H_2O$

Hydrated $CrCl_2.H_2O$ (10 gms) was refluxed with 50 ml of $SOCl_2$ for several hrs. The dehydrated salt was collected by distillation and evaporated in vacuum.

Dehydration of $FeCl_2.6H_2O$

10 gms of Fe(II)hexahydrate in 60 ml of acetic anhydride was refluxed for 3 hrs. The compound then filtered, washed several times with acetic anhydride followed by $SOCl_2$ and vacuum dried.

Preparation of Dichlorobis (triphenylphosphine) cobalt (II)[67]

An excess of triphenylphosphine (1.5 times the stoichiometric amount) was melted on a water bath and $CoCl_2.6H_2O$ was

slowly added to this molten triphenylphosphine with continuous magnetic stirring. The reaction mixture was stirred for 5-10 minutes. After that cooled and ground in a mortar, the blue crystalline product obtained was recrystallized from hot ethanol (m.p. 225°C).

Preparation of chlorotris(triphenylphosphine) Copper(I)[67]

25 m mol (6.55 gm) triphenylphosphine was dissolved in 100 ml $CHCl_3$ in which 6.5 m mol (0.6015 gm) CuCl was added in portions with continuos stirring, and then dry 400 ml ethanol was added followed by vigorous stirring for 2 hrs. A shining white microcrystalline solid separated out was collected (m.p. 150-160°C).

Preparation of Dichlorobis(triphenylphosphine) Nickel (II)[68]

5 m mol (1.19 gm) $NiCl_2.6H_2O$ was dissolved in 25 ml glacial acetic acid and 10 m mol (2.62 gm) triphenylphosphine in 50 ml glacial acetic acid was added. The olive green microcrystalline mass precipitates out, when kept in contact with its mother liquor for 24 hrs gave dark green crystals which were filtered off, washed with glacial acetic acid and vacuum dried (m.p. 244°C).

Preparation of Dichlorobis(triphenylphosphine) Mercury (II)[69]

A solution of triphenylphosphine (1.1 gm, 2 mol) and mercuric chloride (0.5 gm, 1 mol) both in hot alcohol (50 cm^3

and 25 cm^3 respectively) were rapidly mixed and allowed to cool. White crystals of the product was filtered, dried in vaccum desicator (m.p. 273°C).

Preparation of Dichlorobis(triphenylphosphine) Cadmium (II)[69]

2 m mol (10 gm) triphenylphosphine and 1 mol of cadmium chloride (15 gm) in water (50 cc) were vigorously shaken together and the crystalline precipitate was collected, drained and recrystallized from ethanol (m.p. 134°C).

Preparation of Dichlorobis(triphenylphosphine) Zinc (II)[70]

The solution of anhydrous $ZnCl_2$ (0.6814 gm) in ether had been added to the triphenylphosphine solution in dry benzene 10 m mol (2.6229 gm). White shining crystals were slowly precipitated out (m.p. 336°C).

Preparation of Dichlorobis(triphenylphosphine) Mn(II)[71]

Anhydrous $MnCl_2$ (3.1 gm) was dissolved in dry t.h.f. followed by the addition of triphenylphosphine (5.25 gm). The reaction mixture was refluxed for 3 hrs. The final product was then precipitated by adding diethylether and then filtered (m.p. 232°C).

Preparation of Cuprous chloride[72]

A mixture consisting of1part of $CuSO_4.5H_2O$, two parts of

NaCl and one part of copper turnings was heated with ten parts of H_2O until the color disappear completely. The mixture was poured into water, and CuCl crystallize out as white crystalline solid which has been dried and stored in vacuum.

Preparation of $[Ag(PPh_3)_3Cl]$[73]

0.998 gm (6.5 m mol) silver chloride dissolved in a mixture of acetonitrite and 20 ml of methanol was added all at once to 6.55 gm (25 m mol) triphenylphosphine in 50 ml of methanol, crystals of $[Ag(PPh_3)_3Cl]$ were formed after some time and were collected after standing at room temperature overnight (m.p. 197°C).

Preparation of Chlorotris(triphenylphosphine) Cobalt(I)[74] :

15 m mol (3.93 gm) triphenyl phosphine was dissolved in 100 ml $CHCl_3$ in which 5 m mol (0.65 gm) $CoCl_2$ was added in portion with continuos stirring and then dry 200 ml ethanol was added followed by vigorous stirring for 2 hrs. A stable, green, crystalline solids seperated out (m.p. 176°C).

Reaction of H3,4$(CN)_2$5NH_2pz with Anhydrous Metal(II)chlorides, MCl_2; Synthesis of Dichlorotetrakis(3,4-dicyano-5-aminopyrazole) Metal(II), $[ML_4Cl_2]$, [M = Cr(1a), Mn(2a), Fe(3a), Co(4a), Ni(5a), Cu(6a); L = H3,4$(CN)_2$5NH_2pz].

An alcoholic solution ($\sim$35 cm^3) of the ligand (0.05 mol)

was slowly added with the help of droping funnel to anhydrous metal chlorides (0.01 mol) dissolved in t.h.f. ($\sim$50 cm^3) at room temperature and stirred for about 4 hrs. The product was filtered, washed several time with alcohol followed by ether and dried in vacuo. Yield-1a(70%), 2a(82%), 3a(75%), 4a(85%), 5a(78%), 6a(85%).

Reaction of H3,4$(CN)_2$5NH_2pz with [$M(PPh_3)_2Cl_2$]; Synthesis of Dichlorotetrakis(3,4-dicyano-5-aminopyrazole) Metal(II), [ML_4Cl_2] [M = Mn(2a'), Co(4a'), Ni(5a'), Cu(6a')]

0.01 mol of precursor, [$M(PPh_3)_2Cl_2$] dissolved in $\sim$70 cm^3 of t.h.f. was reacted with 0.05 mol of ligand solution dissolved in $\sim$50 cm^3 of EtOH, in a closed reaction vessel. The reaction mixture was stirred for about 2 hrs. The compound formed was filtered, washed with ether and dried in vacuo. The mother liquor left 2 mol equivalent colorless microcrystalline solid identified as Ph_3P on the basis of micro analysis, melting points and i.r. spectral studies. Yield - 2a' (76%), 4a' (88%), 5a'(90%).

Reaction of H3,4$(CN)_2$5NH_2pz with Group IIB Metal (II) Chlorides; Synthesis of Dichlorotetrakis (3,4-dicyano-5-aminopyrazole) Metal (II), [ML_4Cl_2] [M = Zn (7a), Cd (8a), Hg (9a)].

An alcoholic solution ($\sim$40 cm^3) of ligand (0.045 mol) was reacted slowly with 0.01 mol of MCl_2 solution in $\sim$60 cm^3 ethanol at room temperature. The content was stirred for several

hours resulting in the formation of the colorless solid product. The solid thus formed was washed several times with EtOH followed by ether and dried in vacuo. Yield 7a (72%), 8a (88%), 9a (79%).

Reaction of Triphenylphosphine Derivatives of Group IIB Metal Chlorides $[M(PPh_3)_2Cl_2]$ with $H3,4(CN)_25NH_2pz$; Synthesis of Dichlorotetrakis(3,4-dicyano-5-aminopyrazole) Metal(II), $[ML_4Cl_2]$ [M = Zn(7a'), Cd(8a'), Hg(9a')]

0.01 mol ligand solution in 60 cm^3 ethanol was slowly added to 0.045 mol solution of $[M(PPh_3)_2Cl_2]$ taken in 50 cm^3 of alcohol at room temperature. The reaction mixture on mechanical stirring for 7 hrs. resulted in the formation of colorless solid products. The solid product formed was washed several time with ethanol followed by ether. The mother liquor left colorless microcrystalline solidequivalentto 2 mols identified as triphenylphosphine on the basis of elemental analysis and i.r. spectral data. Yield 7a' (80%), 8a' (72%), 9a' (85%).

Reaction of $H3,4(CN)_25NH_2pz$ with Metal (I) Chlorides; Synthesis of 1,2-dihapto 3,4-dicyano-5-aminopyrazolido Metal (I) Oligomer $[M(3,4(CN)_25NH_2pz)]_n$ [M = Cu(I), Ag(I)].

A 0.02 mol ammonical solution of MCl ($\sim$50 cm^3) has been reacted with 0.025 mol solution of $H3,4(CN)_25NH_2pz$ taken in 40 cm^3 ethanol. The reaction mixture was stirred mechanically for several hours resulting in the formation of colorless sticky

product. The product was washed several times with EtOH followed by ether causing no change in its polymeric nature. The product was found insoluble in most of polar and nonpolar solvents.

Reaction of $H3,4(CN)_2 5NH_2pz$ with Triphenylphosphine Derivatives of Co(I), Cu(I) and Ag(I); Synthesis of Bis(1,2-dihapto 3,4-dicyano-5-aminopyrazolido)bis (triphenylphosphine) Metal (I), $[M(PPh_3)_2\ (H3,4(CN)_2 5NH_2pz)]_2$.

A solution of ligand (0.025 mol) in ethanol ($\sim$ 50 cm^3) was poured to an ammonical solution of $[M(PPh_3)_3Cl]$ [M = Co(I), Cu(I) and Ag(I)] (0.021 mol). The resulting colorless solid mass formed was filtered, washed with ethanol and then with ether and finally dried in vacuo. The mother liquor along with the ethanol and ether washing left colorless microcrystalline solid which has been identified as triphenylphosphine on the basis of micro-analysis, melting points and i.r. spectral data (Table 4 and 5).

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The ligand 3,4-dicyano-5-aminopyrazole, $H3,4(CN)_2 5NH_2pz$ [Fig. (VIII)] act as 2-monohapto ligand coordinating to the metal ion via pyridyl nitrogen N(2) in neutral reaction medium. However, it acts as an uninegative, exobidentate 1,2-dihapto ligand [Fig. (IX)] in basic reaction medium called 3,4-dicyano 5-aminopyrazolide ion $[3,4(CN)_2 5NH_2pz]^-$. In view of C_{2v} symmetry of $[3,4(CN)_2 5NH_2pz]^-$, it may coordinate through both the nitrogen N(1), as well as N(2) and acts as a bridging ligand between two similar metal ion producing dimeric compounds.

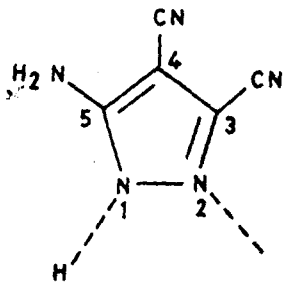


Fig.(VIII)

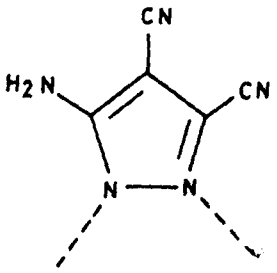


Fig.(IX)

The reaction of H3,4-dicyano-5-aminopyrazole $H3,4(CN)_2 \cdot 5NH_2pz(L)$ with MCl_2 in t.h.f. at room temperature resulted in the isolation of solid products having stoichiometry as $[ML_4Cl_2]$ [M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II)] based on elemental analysis (Table 1).

Table 1. Elemental Analyses, Molecular Weights and Molar Conductivity Values of the Complexes.

Complexes	Lable	Yield (%)	Found (Calcd) (%)					Mol. Wt. Found (Calcd.)	Molar Conductvity $cm^2\ ohm^{-1}\ mol^{-1}$
			M	Cl	C	H	N		
$CrC_{20}H_{12}N_{20}Cl_2$	(1a)	83	7.44 (7.65)	10.71 (10.87)	35.7 (36.7)	1.80 (1.83)	42.72 (42.87)	648.5 (653)	19.4
$MnC_{20}H_{12}N_{20}Cl_2$	(2a)	78	7.9 (8.07)	10.9 (10.82)	35.0 (36.5)	1.80 (1.82)	42.0 (42.78)	649 (656)	21.6
$MnC_{20}H_{12}N_{20}Cl_2$	(2a')	85	7.5 (8.07)	10.75 (10.82)	35.3 (36.5)	1.84 (1.82)	42.3 (42.78)	646 (656)	22.0
$FeC_{20}H_{12}N_{20}Cl_2$	(3a)	76	8.02 (8.21)	10.7 (10.81)	35.1 (36.5)	1.81 (1.82)	41.9 (42.6)	647 (657)	24.1
$CoC_{20}H_{12}N_{20}Cl_2$	(4a)	81	8.51 (8.63)	10.6 (10.75)	36.18 (36.36)	1.80 (1.81)	42.3 (42.4)	650.5 (660)	29.0
$CoC_{20}H_{12}N_{20}Cl_2$	(4a')	76	8.72 (8.63)	10.65 (10.75)	36.21 (36.36)	1.80 (1.81)	42.0 (42.4)	648.5 (660)	23.5
$NiC_{20}H_{12}N_{20}Cl_2$	(5a)	79	8.61 (8.70)	10.62 (10.74)	36.15 (36.33)	1.80 (1.81)	42.21 (42.39)	651 (660.5)	19.0
$NiC_{20}H_{12}N_{20}Cl_2$	(5a')	82	8.59 (8.70)	10.65 (10.74)	36.21 (36.33)	1.80 (1.81)	42.19 (42.39)	649 (660.5)	21.5
$CuC_{20}H_{12}N_{20}Cl_2$	(6a)	80	9.10 (9.25)	10.51 (10.68)	36.17 (36.11)	1.82 (1.80)	42.25 (42.13)	655.5 (664.5)	24.0
$CuC_{20}H_{12}N_{20}Cl_2$	(6a')	77	9.15 (9.25)	10.53 (10.68)	36.15 (36.11)	1.81 (1.80)	42.20 (42.13)	657 (664.5)	21.0

Contd.....

$ZnC_{20}H_{12}N_{20}Cl_2$	(7a)	85	9.40 (9.52)	10.49 (10.65)	36.3 (36.0)	1.77 (1.80)	42.3 (42.0)	654.5 (666.5)	23.0
$ZnC_{20}H_{12}N_{20}Cl_2$	(7a')	82	9.42 (9.52)	10.51 (10.65)	35.5 (36.0)	1.79 (1.80)	41.8 (42.0)	656.5 (666.5)	22.0
$CdC_{20}H_{12}N_{20}Cl_2$	(8a)	79	15.31 (15.48)	9.81 (9.95)	36.53 (36.63)	1.65 (1.68)	39.1 (39.24)	702.0 (713.5)	25.0
$CdC_{20}H_{12}N_{20}Cl_2$	(8a')	83	15.37 (15.48)	9.85 (9.95)	36.53 (36.63)	1.66 (1.68)	39.0 (39.24)	705.0 (713.5)	26.0
$HgC_{20}H_{12}N_{20}Cl_2$	(9a)	80	16.31 (16.42)	9.73 (9.84)	33.11 (33.26)	1.61 (1.66)	38.65 (38.80)	712.0 (721.5)	23.0
$HgC_{20}H_{12}N_{20}Cl_2$	(9a')	83	16.34 (16.42)	9.75 (9.84)	33.33 (33.26)	1.60 (1.66)	38.55 (38.80)	714.0 (721.5)	25.0

The compound having composition $[ML_4Cl_2]$ were also formed by reacting $[M(PPh_3)_2Cl_2]$ [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)] with H3,4-dicyano-5-amino-pyrazole in t.h.f. at room temperature. The liberated PPh_3 equivalentto two mol has been recovered as colorless micro-crystals from the filtrate and etherial washings when evaporated in vacuum as shown below.

$$[M(PPh_3)_2Cl_2] + 4L \longrightarrow [ML_4Cl_2] + 2PPh_3 \quad \ldots (6)$$

(M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)

The reaction of 3,4-dicyano-5-aminopyrazole with ammonical solution of MCl. (M = Cu, Ag) resulted in the formation of polymeric compounds having composition $[ML]_n$. However, the reaction with ammonical solution of $[M(PPh_3)_3Cl]$(M = Co, Cu and Ag) resulted in the formation of dimeric species of the type $[M(PPh_3)_2L]_2$ as shown below :

$$2[M(PPh_3)_3Cl] + 2L \longrightarrow [M(PPh_3)_2L]_2 + 2PPh_3 \quad \ldots (7)$$

[M = Co(I), Cu(I), Ag(I)]

The liberation of PPh_3 in eq. (7) has been isolated by evaporating the filtrate and washings in vacuum. (Expt.Section).

The i.r. spectrum of pyrazole with complete assignments is well documented in literature[7,28a,28b,48,49] for different

mode of bonding of the ligand. The i.r. spectrum of the ligand H3,4$(CN)_2$5NH_2pz (Table-2) exhibits bands comparable to those reported[7,28a,28b,48,49] for pyrazole ligand. The N-H stretching appears at considerably lower wavelength attributable to intra or intermolecular hydrogen bonding[6,7]. However, the N-H bending vibration reported[75] for the solid pyrazole ligand have not been seen in the present ligand. The vibrations associated to the pyrazole ring such as ring vibrations (R_1, R_2, R_3 and R_4) appear at their estimated positions. The C-H stretching and C-H bending vibrations too appear at the expected positions. The band appearing at 1490 cm^{-1} as a medium intensity band may presumbaly be assigned for -C=N stretching vibration consistent with the free benzopyrazole[53]. A very strong band at 2250 cm^{-1} may reasonably be assigned for -C≡N stretching vibration analogous to that reported[54-56] for tne free -C≡N group. However, a multiplet (three medium to strong intensity bands) in the region 3300-3400 cm^{-1} alongwith a strong band at 1610 cm^{-1} may be assigned for NH_2 group vibrations.

The bands observed in the i.r. spectra of the complexes either obtained from anhydrous metal chlorides or their triphenylphosphine derivatives (Table-2) were compared with the free ligand vibrations. The remarkable features of the spectra show bands corresponding to -C=N and NH_2 groups which have appeared in the same frequency regions as recorded for free ligand,

Table-2. Infrared Vibrational Frequencies (cm^{-1}) of the Ligand and the Complexes.

Compounds	N-H str. (Pyrollic)	NH_2 str.	C-H str. C-H bending	Ring Vibrations	C=N	M-N	M-Cl
Ligand(L)	2910s	3400s 3350s 3300s 1610vs	3140s 1060s 1040s 870m	1480s 1380s 1340s 930m	2250vs		
(1a)	3420s	3410s 3355s 3310m 1610vs	3150m 3130sh 1050s 830m	1470s 1390m 1360sh 950m	2250vs	235s	285m
(2a)	3435s	3405s 3350s 3315s 1610vs	3155m 3130sh 1055s 1025m 835m	1465s 1380m 1365sh 945m	2250vs	230s	280m
(2a')	3430s	3410s 3355s 3315s 1610vs	3160m 3140sh 1050s 1025m 825m	1470s 1380m 1360sh 940m	2250vs	230s	280m
(3a)	3425s	3415s 3350s 3310s 1610vs	3150m 3130sh 1055s 825m	1475s 1380m 1365sh 945m	2250vs	235s	285m
(4a)	3420s	3440s 3350s 3315s 1610vs	3140s 3130sh 1050m 1030m 830m	1480s 1385m 1360sh 940m	2250vs	230s	280m
(4a')	3430s	3405s 3350s 3315s 1610vs	3150m 3130sh 1050s 1025m 830m	1460s 1380m 1365sh 945m	2250vs	230s	290m
(5a)	3420s	3410s 3355s 3310m 1610vs	3150m 3130sh 1055s 1030m 830m	1470s 1385m 1360sh 950m	2250vs	220s	280m
(5a')	3425s	3415s 3360s 3315m 1610vs	3155m 3135sh 1050s 830m	1475s 1380m 1360sh 950m	2250vs	230s	285m

(6a)	3430s	3405s 3355s 3315s 1610vs	3155m 3130sh 1050s 1025m 830m	1455s 1380m 1365sh 945m	2250vs	235s	280m
(6a')	3425s	3410s 3350s 3310s 1610vs	3155m 3130sh 1040s 1020m 820m	1560s 1370m 1365sh 940m	2250vs	230s	280m
(7a)	3435s	3410s 3350s 3315s 1610vs	3155m 3130sh 1055s 1025m 830m	1465s 1380m 1365sh 945m	2250vs	230s	275m
(7a')	3430s	3405s 3350s 3315s 1610vs	3150m 3120sh 1050s 1025m 830m	1470s 1480m 1365sh 945m	2250vs	210s	280m
(8a)	3425s	3415s 3360s 3315m 1610vs	3160m 3115sh 1050s 1025m 840m	1465s 1475m 1365sh 945m	2250vs	225s	285m
(8a')	3435s	3410s 3350s 3315m 1610vs	3155m 3115sh 1050s 1025m 830m	1470s 1480m 1365sh 945m	2250vs	230s	285m
(9a)	3430s	3415s 3350s 3310m 1610vs	3160m 3115sh 1050s 1025m 850m	1470s 1480m 1365sh 945m	2250vs	235s	280m
(9a')	3425s	3410s 3350s 3315m 1610vs	3150m 3120sh 1050s 1025m 840m	1470s 1475m 1365sh 940m	2250vs	230s	285m

s = strong, vs = very strong, m = medium, sh = shoulder.

ruling out the possibility of their coordination to the metal ions. However, there is a considerable positive shift in the N-H stretching vibration attributable to differences in the internal or external hydrogen bonding[6,7] indicating the coordination of the ligand via pyridyl nitrogen N(2). This has been further corroborated by a slight negative shift (5-15 cm^{-1}) in the νC=N stretching vibration as reported for benzopyrazole complexes[53].

A strong band in the frequency region 220-235 cm^{-1} may reasonably be assigned as M-N stretching vibration consistent with octahedral complexes derived from the other nitrogen donor ligands[57-59]. However, a medium band in the frequency region 280-290 cm^{-1} has been assigned as M-Cl stretching vibration. The complexes derived from the triphenylphosphine precursors, $[M(PPh_3)_2Cl_2]$ do not show band characteristic of Ph_3P moiety reported[76] to appear Ca 500 cm^{-1}.

The mode of coordination of the ligand and the steriochemistry around the transition metal ions was further confirmed after carrying out magnetic susceptibility measurements and ligand field spectral studies as explained below :

The electronic and reflectance spectra of these complexes are quite comparable suggesting the similar species in the solution as well as in the solid. The observed magnetic moments and a weak band at Ca 15,000 cm^{-1} exhibited by ligand field spectra

may reasonably assigned as $^5T_{2g} \longleftarrow {}^5E_g$ transition (Table-3) are consistent with an octahedral geometry of $[CrL_4Cl_2]$ complex. However, the ligand field spectra of (2a) and (2a') exhibit two bands assignable to $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ transitions respectively. The observed values of magnetic moments further confirm the ground state as $^6A_{1g}$ in the ligand field spectra suggesting an octahedral environment around Mn(II) ions.

A weak absorption band at Ca 12,100 cm^{-1} observed in the ligand field spectra of 3a reasonably corresponds to $^5E_g \longleftarrow {}^5T_{2g}$ transition consistent with the octahedral geometry of the complex[6,7,77]. The observed μeff value further supports the above geometry. However, a shoulder reported[6,7,53] to occur at Ca 10,000 cm^{-1} in other pyrazole complexes could not be recorded in $[FeL_4Cl_2]$ complex.

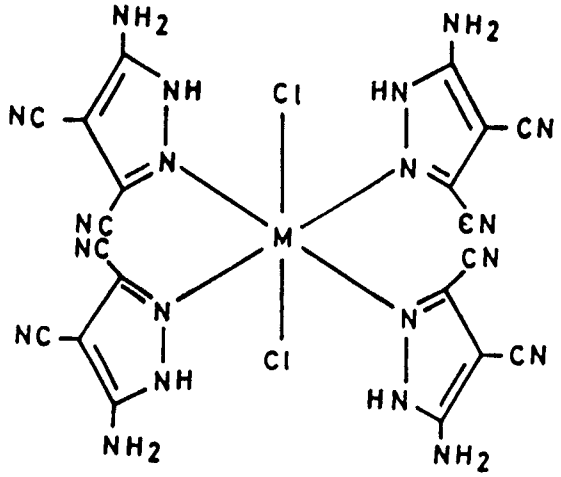
The observed values of magnetic moments for the complexes (4a), (4a'), (5a) and (5a') are slightly higher than that of calculated spin-only values which may be understood in terms of spin orbit coupling contributions[54]. However, the μeff values are quite consistent with spin free Co(II) and Ni(II) octahedral complexes of pyrazoles. The ligand field spectra of (4a) and (4a') exhibit a main band maxima at Ca 20,500 cm^{-1} along with a shoulder appearing at Ca 19,500 cm^{-1} which may reasonably be assigned to the $^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$

Table 3. Magnetic and Ligand Field bands observed in the electronic and reflectance spectra and their assignments of metal complexes.

Complexes	μ eff (B.M.)	Band positions (cm^{-1})	Assignments
(1a)	4.79	15,000 (14,600)	$^5T_{2g} \longleftarrow {}^5E_g$
(2a)	5.95	22,400 (22,300)	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
		18,200 (18,150)	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
(2a')	6.15	22,600 (22,400)	$^4T_{1g}(G) \longleftarrow {}^6A_{1g}$
		18,800 (18,200)	$^4T_{2g}(G) \longleftarrow {}^6A_{1g}$
(3a)	5.45	12,100 (11,950)	$^5E_g \longleftarrow {}^5T_{2g}$
(4a)	4.49	21,450 (21.315)	$^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$
		18,318 (18,210)	$^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$
(4a')	4.52	21,330 (21,215)	$^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$
		18,300 (18,210)	$^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$
(5a)	3.2	27,500 (27.450)	$^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$
		18,100 (17,980)	$^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$
(5a')	3.3	27,777 (27,676)	$^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$
		17,990 (17,690)	$^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$
(6a)	1.8	16,767 (16,600)	$^2T_{2g} \longleftarrow {}^2E_g$
(6a')	1.71	16,930 (16,800)	$^2T_{2g} \longleftarrow {}^2E_g$

Position in $CHCl_3$ Solution given in parentheses.

transitions, respectively confirming an octahedral environment around Co(II) ion. However, two strong ligand field bands recorded at Ca 27,700 cm^{-1} and 17,600 cm^{-1} for (5a) and (5a') complexes correspond to the $^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$ transitions, respectively ascertaining an octahedral environment around Ni(II) ion. The observed magnetic moment and a broad weak band in the electronic spectra of $[CuL_4Cl_2]$ suggest an octahedral geometry (Table-3). The data presented here help us to visualizethe structure of these complexes as given below [Fig.(X)]



M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg.

Fig. (X)

Reaction of 1,2-dihapto-3,4-dicyano-5-aminopyrazolido ion $[3,4(CN)_2 5NH_2pz]^-$ with MCl (M = Cu(I), Ag(I)] and $[M(PPh_3)_3Cl]$ [M = Co(I), Cu(I), Ag(I)]

The reaction of ammonical solution of MCl [M = Cu(I), Ag(I)] with $H3,4(CN)_2 5NH_2pz$ resulted in the formation of colorless compounds. These compounds have been found to be highly insoluble in almost all the polar and non-polar solvents indicating their polymeric nature analogues to that reported[78,79] for $[Cu(pz)]_n$ and $[Ag(pz)]_n$. The i.r. spectral studies on these compounds exhibit the complete absence of N-H stretching vibration expected to appear at 2920 cm^{-1} in free ligand suggesting the formation of 3,4-dicyano-5-aminopyrazolide ion, $[3,4(CN)_2 5NH_2pz]^-$. However, the other bands corresponding to the pyrazole ring and the substituent groups appear at their appropriate positions as recorded for free ligand except a negative shift (10-20 cm^{-1}) in νC=N stretching vibration (Table-4). The absence of νN-H stretching vibration and a slight negative shift in ν C=N stretching vibration suggesting the involvement of both the nitrogens (pyridyl as well as pyrrolic) in bonding. The structure of these compounds could not be established because of the limited physico-chemical studies. However, a possible polymeric structure may be visualized as in Fig.(XI) consistent with $[M(pz)]_n$[77,78] (M = Cu(I), Ag(I)].

Table 4. I.r. Vibrational Frequencies (Cm^{-1})

Compound	ν_{N-H}	ν_{NH_2}	Ring Vibration	ν_{C-H} C-H Bend	$\nu_{C=N}$	$\nu_{C\equiv N}$	ν_{M-N}	Ph_3P	ν_{M-P}
H3,4$(CN)_2$5NH_2pz	2925s	3400s 3350s 3300s 1600vs	1485s 1385s 1345s 940m	3150s 1060s 1040s 875m	1465m	2245vs	230		
[Cu(3,4$(CN)_2$5NH_2pz)]$_n$	-	3410s 3355s 3310m 1610vs	1490s 1385m 1345s 940m	3150s 1060s 1045s 880m	1475m	2250vs	230s	-	-
[Ag(3,4$(CN)_2$5NH_2pz)]$_n$		3405s 3340s 3325s 1610vs	1475s 1375m 1330s 935w	3145s 1070s 1035s 885m	1485m	2250vs	235s	-	-
[Co$(PPh_3)_2$(3,4$(CN)_2$5NH_2pz)]$_2$	-	3400s 3355m 3325s 1615vs	1480s 1390m 1340s 950w	3155s 1070s 1040s 895w	1470m	2250vs	230s	1325s 1080s 730s 510s	310m
[Cu$(PPh_3)_2$(3,4$(CN)_2$5NH_2pz)]$_2$	-	3410s 3350m 3330s 1610vs	1470s 1380m 1345s 945w	3150s 1075s 1040s 890w	1475m	2245vs	220	1430s 1090s 740s 500s	310m
[Ag$(PPh_3)_2$(3,4$(CN)_2$5NH_2pz)]$_2$		3400s 3350m 3310s 1610w	1480s 1375m 1335s 945w	3155s 1065s 1030s 880m	1480m	2250vs	235s	1420s 1080s 730s 500s	320m

s = strong, vs = very strong, m = medium, w = weak.

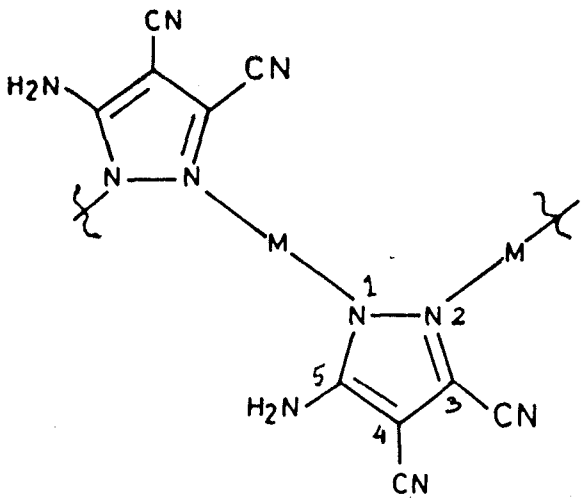


Fig. (XI)

However, the reaction of ammonical solution of triphenylphosphine derivatives of Co(I), Cu(I) and Ag(I), $[M(PPh_3)_3Cl]$ with $H3,4(CN)_25NH_2pz$ afford the isolation of products of the type $[M(PPh_3)_2(3,4(CN)_25NH_2pz)]_2$, [M = Co(I), Cu(I), Ag(I)] liberating Ph_3P equivalent to 1 mol (Experimental section). The compounds are soluble in most of organic solvents. The results of elemental analyses complements the proposed stoichiometry and the molecular weight determination data suggest their dimeric nature (Table-5).

The bands observed in the i.r. spectra indicate the complete absence of the N-H stretching vibration suggesting the deprotonation at pyrrolic nitrogen resulting in the formation of 3,4-dicyano-5-aminopyrazolide ion, $[3,4(CN)_25NH_2pz]^-$. The coordination of pyridyl nitrogen to the metal ions Co(I),

Table 5. Elemental Analyses and Molecular Weights

Compound	Color	Yield	Found (Calcd) (%)				Molecular Weight Found (Calcd.)
			M	C	N	H	
$[Cu(3,4(CN)_2 5NH_2 pz)]_n$	White	78	32.4 (32.9)	30.05 (30.69)	35.15 (35.88)	1.0 (1.02)	-
$[Ag(3,4(CN)_2 5NH_2 pz)]_n$	White	82	44.85 (44.95)	24.5 (25.02)	29.31 (29.19)	0.83 (0.83)	-
$[Co(PPh_3)_2(3,4(CN)_2 5NH_2 pz)]_2$	Lightblue	73	8.15 (8.25)	68.0 (68.8)	9.9 (9.79)	4.31 (4.47)	1429.1 (1430.0)
$[Cu(PPh_3)_2(3,4(CN)_2 5NH_2 pz)]_2$	Yellowish White	79	8.72 (8.82)	65.8 (65.8)	9.62 (9.72)	4.31 (4.41)	1438.1 (1439.0)
$[Ag(PPh_3)_2(3,4(CN)_2 5NH_2 pz)]_2$	Light yellow	81	13.9 (14.2)	61.5 (62.0)	8.61 (9.1)	3.9 (4.1)	1527.1 (1527.6)

Cu(I) or Ag(I) has been indicated by negative shift (~10-21 cm^{-1}) in νC=N stretching vibration (Table-4). The presence of Ph_3P groups acting as endcapping groups avoid the polymerization of these compounds has been evidenced by the characteristic bands corresponding to Ph_3P moiety. However, the bands arising from the ring vibrations and substituents CN and NH_2 do not undergo any change and appear at their appropriate positions suggesting the $[3,4(CN)_2 5NH_2 pz]^-$ ion coordinates via both the nitrogens pyrrolic N(1) and pyridyl N(2). [Fig.(XII)].

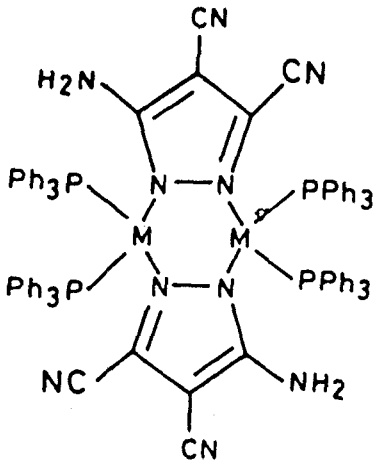


Fig.(XII)

REFERENCES

REFERENCES

1. S. Trofimenko, Adv. Chem. Ser., 150, 289 (1976).

2. R.J. Sundberg, D.C. Mente and I. Yilmaz, J. Heterocycl. Chem., 14, 1279 (1977).

3. H.M.J. Hendriks and J. Reedijk, Inorg. Chim. Acta., 37, L 509 (1979).

4. N.A. Daugherty and J.H. Swisher, Inorg. Chem., 7, 1657 (1968).

5. J. Reedijk, Rectl. Trav. Chim., Pays-Bas, 89, 605 (1970).

6. J. Reedijk, W.L. Driessen and W.L. Groeneveld, ibid, 88, 1095 (1969).

7. J. Reedijk, ibid, 88, 1451 (1969).

8. J. Reedijk, ibid, 89, 993 (1970).

9. C.W. Reiman, A. Santoro and A.D. Mighell, Acta. Crystallogr., Sec. B, 16, 521 (1970).

10. C.W. Reiman, Chem. Commun., 146 (1969).

11. A.D. Mighell, C.W. Reiman and A. Santoro, Acta. Crystellogr Sec. B, 25, 595 (1969).

12. S. Trofimenko, Chem. Rev., 72, 501 (1972).

13. J. Reedijk, Recl. Trav. Chim., Pays-Bas, 88, 1451 (1969).

14. D. Nichols and B.A. Warburston, J. Inorg. Nucl. Chem., 33, 1041 (1971).

15. M. Inoue, M. Kishita and M. Kubo, Inorg. Chem., 4, 629 (1965).

16. J. Reedijk, J.C.A. Windhorst and N.H.M. Van Ham, Recl. Trav. Chim., Pays-Bas, 90, 234 (1971).

17. S.N. Poddar, Sci. Cult (Culcutta) 35, 28 (1969); Chem. Abstr., 71, 66820q (1969).

18. C.W. Reiman, J. Pys. Chem., 74, 561 (1970).

19. F. Kralik and J. Vrestal Collect. Czech. Chem. Commun., 27, 1653 (1962).

20. F. Kralik and J. Vrestd., ibid, 26, 1298 (1961).

21. S.G. Matsoyan, E.G. Darbinian and Y.B. Mitardzhyan Khim. Zh, 21, 998 (1968), Index Chemicus, No. 112246 (1969).

22. D.J.O. Sullivan and F.J. Lalor, J. Org. Metal. Chem., 25, C 80 (1970).

23. A. Bond and M. Green, J. Chem. Soc., A, 682 (1971).

24. F. Seel and V. Sperber, Angew Chem., 80, 38 (1968).

25. V.N. Babin, L.A. Fedorov, N.S. Kochetkova and Yu. A. Belousov, Abstracts of the Fifth International Conference on Organometallic Chemistry, Moscow, USSR, 1971, paper 390, Vol. II, p.429.

26. A.D. Garnovskii, N.E. Kolobova, I.B. Ziotina, G.K. Mitina, K.N. Anisomov and O.A. Osipov, ibid, 1971, paper 108, Vol. I, p. 291.

27. H.H. Murry, Raphael, G. Rapits, and John P. Fackler, Inorg. Chem., 27, 26 (1988).

28a. M. Shakir, D. Kumar and Z.A. Siddiqi, Indian Journal of Chem., 29A, 919 (1990).

28b. M. Shakir, D. Kumar and Z.A. Siddiqi, Synth-React. Inorg. Met.-Org. Chem., 29(9), 1241 (1990).

29. E. Buchner, Chem. Ber. 22, 2165 (1889); H. Reimlinger, A. Noels, J. Jabot, V-over Straeten, A. Chem. Ber., 103, 1942 (1970).

30. J.G. Vos and W.L. Groeneveld, Transition Met. Chem., (Weinhein, Ger.), 4, 137 (1979).

31. H. Okkersen, W.L. Groeneveld and J. Reedijk, Recl. Trav. Chim., Pays-Bas, 92, 945 (1973).

32. M. Shakir, D. Kumar and Z.A. Siddiqi, Transition Met. Chem., 16, 631 (1991).

33. J. Bielawski and K. Niedenzu, Inorg. Chem., 25, 85 (1986).

34. J. Bielawski and K. Niedenzu, ibid, 25, 1771 (1986).

35. S. Trofimenko, J. Am. Chem. Soc. 91, 5410 (1969).

36. E.M. Holt, S.L. Holt, K.J. Watson and B. Olsen, Cryst. Struct. Commun., 7, 613 (1978).

37. J. Bielawaski, M.K. Das, E. Hanecker, K. Niedenzu and H. North, Inorg. Chem., 25, 4623 (1986).

38. C. Habben, L. Komorowski, W. Maringgek, A. Meller and K. Niedenzu, ibid, 28, 2659 (1989).

39. S. Trofimenko, Acc. Chem. Res., 4, 17 (1974).

40. M. Green, J.A.K. Howard, A.P. James, C.M. Nunn and F.G.A. Stone, J. Chem. Soc. Dalton Trans., 187 (1986), S.H.F. Becke, M.D. Bermudez, N.H. TranHuy, J.A.K. Howard, O. Johnson and F.G.A. Stone, ibid, 1229 (1987).

41. Jozef Kozisek, Maria Hvastijova, Jiri Kohout, Jerzy Mrozinski and Helmut Kohlev, J. Chem. Soc. Dalton Trans., 1773 (1991).

42. C.W. Eigenbrot and K.N. Raymond, Inorg. Chem., 20, 1553 (1981).

43. C.W. Eigenbrot and K.N. Raymond, ibid, 21, 2653 (1982).

44. H. Schumann, P.R. Lee and J.Loebel, Angew. Chem., Int. Ed. Engl., 28, 1033 (1989).

45. G. Biekng, Doktordes Fachbereiches Chemie Thesis, University of Hamburg (1979).

46. R.D. Fischer, E. Klahne, J.Z. Kopf and B. Naturforsch, Anorg. Chem., Org. Chem., 33B, 1393 (1978).

47. W. Charles, J.R. Eigenbrot and Kenneth N. Raymond, Inorg. Chem., 21, 2653 (1982).

48. R.J. Carlson and T.L. Brown, Inorg. Chem., 5, 268 (1966).

49. H. Zimmermann, Z. Elektrochem., 65, 821 (1961).

50. C.W. Reimann, J. Pays-Chem., 74, 561 (1970).

51. C.W. Reimann and A.B. Mighell, ibid, 71, 2375 (1967).

52. D.J. Doonan and D.L. Bloch, J. Am. Chem. Soc., 97, 1403 (1975).

53. S.P. Ghosh and L.K. Mishra, J. Indian Chem. Soc., 47, 1154 (1970).

54. R.J.H. Clark, J. Lewis, D. Machin and R.S. Nyholm, J. Chem. Soc., 397 (1963).

55. K.F. Prucell and R.S. Drago, J. Am. Chem. Soc., 88, 919 (1966).

56. R.A. Walton, Quart. Rev., 19, 126 (1965).

57. L. Sacconi, A. Sabatini and P. Gans, Inorg. Chem., 3, 1772 (1964).

58. J. Reedijk and D.W.L. Groeneveld, Recl. Trav. Chim. Pays-Bas; 87, 1079 (1968).

59. D.H. Brown, R.H. Nuttall, J. McAvoy and D.W.A. Sharp, J. Chem. Soc., 892 (1966).

60. A. Sebatini and L. Sacconi, J. Am. Chem. Soc., 86, 17 (1964).

61. F.G. Mann and B.C. Saunders 'Practical Organic Chemistry' Longmans London, 435 (1961).

62. I.M. Kolthoff, E.B. Sandell, E.J. Meechan and S. Bruckeustein, 'Quantitative Chemical Analysis', McMillar London, 580 (1969).

63. C.N. Reilley, R.W. Schmid and F.A. Sadak, J. Chem. Edu., 36, 619 (1959).

64. I.A. Korbukh, Yu. N. Bulychiv and M.N. Preobrachenskaya, Khim. Getero. Soedin, 12, 1687 (1979).

65. I. Vogel, 'Text Book of Practical Organic Chemistry' IV Edn., Chapter 2 (1978).

66. G. Brauer, 'Hand Book of Preparative Inorganic Chemistry' Academic Press, New York, London, 2, 1515, 1008 (1965).

67. H.A. Tayim, A. Bouldoukian and F. Award, J. Inorg. Nucl. Chem., 32, 3799 (1970).

68. L.M. Venanzi, J. Chem. Soc., Part 1, 719 (1958).

69. R.C. Evans, F.G. Mann, H.S. Peiser and D. Purdie, J. Chem. Soc. 1209 (1940).

70. G.E. Coats and D. Ridley, J. Chem. Soc., A 166 (1964).

71. L. Naldini, Gazz. Chim. Ital., 90, 1337 (1960).

72. M. Deniges, Comptes Rendus Hebd. Seauces Acad. Sci., 108, 567 (1889).

73. A. Cassel, Acta. Crystallogr., Sect. B, 37, 229 (1981).

74. M. Aresta, M. Rossi and A. Sacco, Inorg. Chim. Acta., 3, 227 (1969).

75. A. Zecchina, L. Cerruti, S. Coluccia and E. Borello, J. Borello, J. Chem. Soc. B., 1363 (1967).

76. K. Nakamoto, Infra-red and Raman Spectra of Inorganic and Coordination Compounds, 3rd Edn., J. Wiley (1978).

77. J. Reedijk, P.W.N.M. Vanleeumen and W.L. Groeneveld, Red. Trav. Chim., Pays-Bas, 87, 129 (1968).

78. S. Trofimenko, Unpublished Results.

79. E. Buchner Ber., 22, 842 (1889).